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Articles

Wormlike Micellar and Vesicular Phases in Aqueous Solutions of Single-Tailed Surfactants with Aromatic Counterions

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The aggregation behavior of a series of alkyltrimethylammonium 5-ethylsalicylate surfactants (C_nTA5ES, $n = 12, 14, 16$) in aqueous solution has been investigated employing turbidity measurements, fluorescence anisotropy experiments (using 3-hydroxynaphthalene-2-carboxylate, HNC^-), and cryo transmission electron microscopy (cryo TEM). Critical aggregation concentrations (cac) were determined by surface tension experiments; they are smaller than those of their salicylate analogues. C_nTA5ES surfactants form vesicles immediately above the cac rather than wormlike micelles such as their salicylate counterparts. C_{12}TA5ES was found to form large unilamellar vesicles (LUVs) which transformed into surfactant layers upon increasing surfactant concentration. The transition was characterized by an increase in turbidity. C_{14}TA5ES and C_{16}TA5ES were found to form LUVs and long wormlike vesicles which are assumed to be responsible for the viscoelasticity of the solutions. Upon increase of the surfactant concentration, a transition to large multilamellar vesicles (LMVs) was observed. In addition, plate structures and elongated vesicles were present. The transition from unilamellar to multilamellar vesicles is accompanied by an increase in turbidity. HNC^- fluorescence anisotropy values (r) were zero below the cac of the surfactants and showed an increase as soon as surfactant aggregates were formed. C_nTA5ES surfactants exhibit temperature-dependent aggregation behavior. Aqueous solutions of C_{16}TA5ES are turbid at low temperatures and undergo a transition to a clear and viscoelastic phase upon increasing the temperature. The turbidity changes are attributed to a vesicle-to-micelle transition.

Introduction

Single-tailed surfactants usually form globular micelles in aqueous solution above their critical micellar concentration (cmc).[1] An increase in surfactant concentration may induce the formation of wormlike micelles.[2] Similarly, addition of organic or inorganic counterions,[2,3] uncharged compounds such as aromatic hydrocarbons,[4] or an oppositely charged surfactant[5] can transform spherical micelles into wormlike micelles. Alkyltrimethylammonium and alkylpyridinium surfactants are the most extensively studied surfactant systems in this respect.[6,7] Halide counterions bind moderately strongly to cationic surfactant aggregates, and therefore, micellar growth is gradual. Upon changing of the counterions to aromatic ones which usually display higher counterion binding, micellar growth already occurs at low surfactant and counterion concentrations.[2,8] However, not only high counterion binding is a prerequisite for micellar growth, but also the orientation of substituents on the aromatic ring is important.[2] ^{1}H NMR studies reveal that $^+N(CH_3)_3$ proton signals are shifted to higher fields and that they are broadened upon addition of salicylate counterions.[9] It was shown that the aromatic ring of salicylate is located between the headgroups and that the OH and COO^- substituents protrude out of the micellar surface.[8,10,11] Theoretical studies showed that wormlike micelles are long and flexible and that they undergo transformations on relatively short time scales.[12] This was confirmed by negative staining[13] and cryo electron microscopy,[14] which

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showed that wormlike micelles can become several hundreds of nanometers in length. The presence of wormlike micelles in aqueous solution is often reflected by an increase in relative viscosity.[1] Upon increase of the surfactant concentration, an entangled network of wormlike micelles is formed which displays viscoelastic behavior. The rheological behavior observed for these surfactant systems is similar to that of solutions of flexible polymers, and therefore, aqueous solutions of entangled wormlike micelles are often called living polymer systems.[6,15] Upon increase of the size of the hydrophobic portion of the counterion, the formation of vesicles has been observed. Lin et al.[16] studied the aggregation behavior of mixtures of hexadecyltrimethylammonium bromide (C_{16}TAB) and 5-methylsalicylic acid. Upon changing of the 5-methylsalicylic acid to C_{16}TAB from 0.1 to 1.1, a gradual change from spherical micelles to vesicles via wormlike and entangled wormlike micellar phases was observed. The results were interpreted in terms of the ratio a_h/a_c, where a_h is the effective headgroup area and a_c the cross-sectional area of the alkyl chain. Addition of 5-methylsalicylic acid to C_{16}TAB leads to a decrease in the ratio a_h/a_c, which explains the morphological change from micelles to vesicles upon changing the c_a/c_s ratio. Also sodium 3-hydroxynaphthalene-2-carboxylate (NaHNC) is able to induce the formation of vesicles in aqueous solutions of C_{16}TAB.[17] This system is compared to catanionic surfactants since the phase behavior shows similarities to that of mixtures of cationic and anionic surfactants. The same system without excess of salt (C_{16}TAHNC) has also been studied. The critical aggregation concentration (cac) of C_{16}TAHNC is 0.03 mM,[18] which is significantly smaller than that of C_{16}TAB (1.0 mM[19]). Aqueous solutions of C_{16}TAHNC show interesting temperature-dependent phase behavior. Upon increase of the temperature, the system undergoes a transition from a turbid vesicular phase to a clear viscoelastic phase containing a network of entangled wormlike micelles. Fluorescence anisotropy and NMR spectroscopy showed an increase in fluidity of the aggregate surface upon increasing the temperature.[20] The phase transition has also been studied by differential scanning calorimetry (DSC) and conductivity experiments.[21] The temperature-induced morphological change has been explained using the theory of phase transitions in a 2D Coulomb gas.[22] It was shown that increasing the temperature results in a decrease of the HNC^- counterion binding; concomitantly the headgroup repulsions between $C_{16}TA^+$ moieties in the bilayer increase which eventually leads to a change in aggregate shape from vesicles to wormlike micelles. A vesicle to micelle transition in aqueous solutions of C_{16}TAHNC can also be induced by shear[23] or by adding C_{16}TAB or NaHNC.[24]

Thus far, most studies have focused on mixtures of C_{16}TAB and *N*-methylsalicylic acid[16] or NaHNC.[17,18,20,21,23,24] Neither the effect of surfactant alkyl chain length on the aggregation behavior nor the phase behavior of the surfactant without salt (eg NaBr) has been investigated in detail. This paper presents a study on the aggregation behavior of alkyltrimethylammonium 5-ethylsalicylate surfactants (C_nTA5ES, where $n = 12, 14, 16$). Cacs have been determined by surface tension measurements. The aggregation behavior has been studied by monitoring the fluorescence anisotropy (r) of HNC^- bound to the surfactant aggregates and by following the turbidity of the samples. The morphology of the aggregates was characterized by cryo transmission electron microscopy (cryo TEM).

Experimental Section

Materials. Cetyltrimethylammonium bromide (C_{16}TAB) was purchased from Merck, C_{14}TAB was from Acros, C_{12}TAB was from Sigma, Dowex (1 × 8 200−400 mesh) and sodium salicylate (NaSal) were from Fluka, and 3-hydroxy-2-naphthoic acid (HNA) and 4-ethylphenol were from Aldrich.

5-Ethylsalicylic Acid (5ESA). 5ESA[25] was synthesized in 51% yield by carboxylation of 4-ethylphenol in *N*,*N*-dimethylacetamide, analogous to a literature procedure for the synthesis of 5-methylsalicylic acid.[26] Mp: 117−118 °C (lit.[25] mp 118−120 °C).

C_nTA5ES. C_nTA5ES surfactants were prepared by addition of equimolar amounts of C_nTAOH to aqueous suspensions of 5ESA. The water was removed by freeze-drying the sample for several days. C_nTAOH surfactants were prepared by exchange of Br^- for OH^- using a Dowex 1 × 8 200−400 mesh column. The eluent was methanol.

C_nTASal. Alkyltrimethylammonium salicylate surfactants (C_nTASal, $n = 12, 16$) were prepared by exchange of Br^- for Sal^- on a Dowex 1 × 8 200−400 mesh column using methanol as the eluent.

Sodium 3-Hydroxynaphthalene-2-carboxylate (NaHNC). An aqueous solution of NaHNC was prepared by stirring the corresponding acid in water containing an equimolar amount of sodium bicarbonate at 50 °C for 5 h.

Cac measurements. Cacs of C_nTA5ES were measured using a TVT 1 Lauda drop tensiometer at 30 °C. The water used was doubly distilled. Cacs were determined in duplicate, and each measurement covered about 15 points in the concentration range from about 0.1 times the cac to 10 times the cac. The measured surface tension is the average of 4−5 drop cycles. Cacs of C_{12}TASal and C_{16}TASal were determined by conductivity experiments using a Wayne-Kerr B642 Autobalance Universal bridge fitted with a Philips PW9512101 electrode. Solutions in the conductivity cell were stirred magnetically and thermostated at the desired temperature. Conductivities were corrected for volume changes.

Fluorescence Anisotropy Experiments. Fluorescence anisotropy measurements were performed on an SLM Aminco spectrofluorometer equipped with a polarization device and a thermostated cell holder. The fluorescence anisotropy (r) was calculated using eq 1.

$$r = \frac{I_{vv} - I_{vh}}{I_{vv} - 2I_{vh}} \quad (1)$$

Herein, I_{vv} and I_{vh} denote the fluorescence intensities when the system is excited by vertically polarized light and the emission monitored through a vertical and a horizontal polarizer, respectively. The excitation and emission wavelengths of HNC^- were 380 and 520 nm, respectively. The excitation and emission band-

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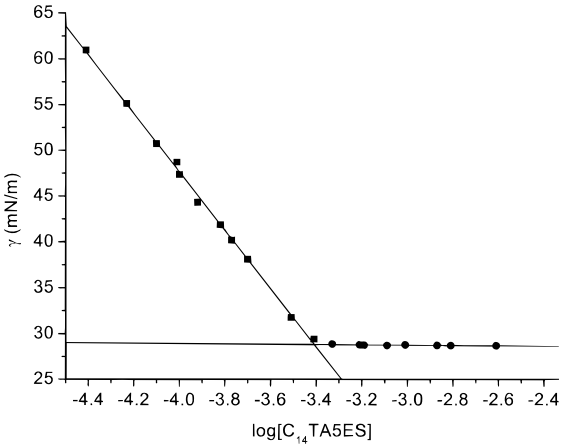

Figure 1. Dependence of the surface tension on the concentration of C_{14}TA5ES at 30 °C.

Table 1. Critical Aggregation Concentrations (Cacs) and Surface Tension Values at the Cac (γ_{cac}) of C_nTA5ES and C_nTASal Surfactants

	cac (mM)		γ_{cac} (mN m^{-1})	
n	C_nTA5ES	C_nTASal	C_nTA5ES	C_nTASal
12	1.38	3.0	28	31
14	0.40	0.69[28]	29	*a*
16	0.098	0.16	30	32

[a] Not determined.

passes were 5 and 2.5 nm, respectively. Experiments were performed at 30 °C.

Turbidity Measurements. Turbidity experiments were performed on a Philips PU 8740 UV/vis spectrophotometer equipped with a magnetic stirring device and a thermostated cell holder. Turbidity is expressed as the optical density at 400 or 450 nm in the presence of HNC^-.

Electron Microscopy. Aliquots of surfactant solutions were deposited on holey carbon grids; the excess solution was blotted off using filter paper. The samples were vitrified by plunging them into liquid ethane. The grids were transferred to a Gatan model 626 cryo holder and examined at ca. −170 °C in a CM10 or CM120 microscope (Philips) operating at 100 or 120 kV. Micrographs were recorded under low dose conditions.

Results and Discussion

Drop Tensiometry. Cacs of C_nTA5ES have been determined by drop tensiometry. Figure 1 shows the dependence of the surface tension on the concentration of C_{14}TA5ES. The break in the plot corresponds to the cac. Surface tension measurements are sensitive to impurities.[27] The absence of a minimum in the surface tension plot suggests a high purity of the used surfactants. Similar plots were obtained for C_{12}TA5ES and for C_{16}TA5ES. Table 1 presents the cacs of C_nTA5ES surfactants and of the corresponding salicylate surfactants. The latter were determined by conductivity experiments and are in agreement with literature values.[28] As expected, cacs of C_nTA5ES surfactants decrease upon increasing chain length (n) and are smaller than those of their salicylate analogues. Equation 2 relates the cac to the number of

$$\log(\text{cac}) = A - Bn \tag{2}$$

carbon atoms in the alkyl chain.[29] A and B reflect the Gibbs energy changes involved in transferring the headgroup and a methylene group from the aqueous phase to the micellar phase, respectively. B equals 0.3 which is comparable to literature values for alkyltrimethylammonium bromides and other ionic surfactants.[29]

The area per surfactant in the monolayer (a_s) can be estimated using the Gibbs isotherm for a 1:1 electrolyte[29]

$$\Gamma = \frac{1}{2RT}\frac{d\gamma}{d(\ln c)} = \frac{1}{4.606RT}\frac{d\gamma}{d(\log c)} \tag{3}$$

$$a_s = \frac{1}{\Gamma N_a} \tag{4}$$

in which Γ is the surface excess (mol m^{-2}), R is the gas constant, T is the absolute temperature, c is the surfactant concentration, and N_a is Avogadro's number. The areas at the air−water interface for C_{12}TA5ES and C_{14}TA5ES are estimated to be 64 and 62 Å^2, respectively; a_s for C_{16}TA5ES was irreproducible. The areas at the air−water interface for C_{12}TA5ES and C_{14}TA5ES are in agreement with earlier studies which report a_s values for C_nTAB ranging from 60 to 75 Å^2.[30] Eastoe et al.[31] studied *n*-alkylammonium dodecylsulfates in which the alkyl group is propyl, butyl, hexyl, and heptyl. In that study the mean area per hydrocarbon chain is around 30 Å^2; the values were calculated by deviding the areas (as calculated from eqs 3 and 4) by 2. In our case this treatment is not warranted since it is not known to what extent both ions contribute to a_s. However, it seems reasonable to assume that the area per surfactant chain (C_nTA^+) is smaller than 64 and 62 Å^2 for C_{12}TA5ES and C_{14}TA5ES, respectively, due to penetration of the $5ES^-$ ion between the headgroups of the surfactant molecules, analogously to salicylate.[8,10,11] In this way the cationic headgroup repulsions are reduced, hydration water is (partly) released, and subsequently the cationic headgroups occupy smaller headgroup areas as compared to, for example, C_nTAB.

The surface tensions at the cac (γ_{cac}) for C_nTA5ES and C_nTASal surfactants are also shown in Table 1. The γ_{cac} values of C_nTA5ES are relatively low as compared to that for C_nTASal and other cationic micelle forming surfactants which usually show values in the range of 30−40 mN m^{-1}.[30] This is in agreement with a close packing of the surfactants at the air−water interface. Surface tension values at the cac of C_{12}TASal and C_{16}TASal are of the same order of magnitude.

Aggregation Behavior of C_nTA5ES. Upon increase of the C_nTA5ES concentration in water, different types of aggregates are formed. The aggregation behavior was studied by monitoring the turbidity of the solutions and the HNC^- fluorescence anisotropy which provides information on the molecular motions of the probe.[32] HNC^- shows significant fluorescence anisotropy when bound to surfactant aggregates due to hindered rotational motion of the probe. The fluorescence spectrum of HNC^- does not interfere with that of $5ES^-$. Since HNC^- is a strongly binding counterion, it is expected to be located at the surface of aggregates formed by C_nTA5ES. This also implies that HNC^- will compete with $5ES^-$ for binding sites; therefore, it might influence the aggregation behavior of C_nTA5ES. To minimize the effect of of HNC^- on the aggregates formed by C_nTA5ES, the HNC^- concentration was kept as low as 50 μM. It is possible to measure

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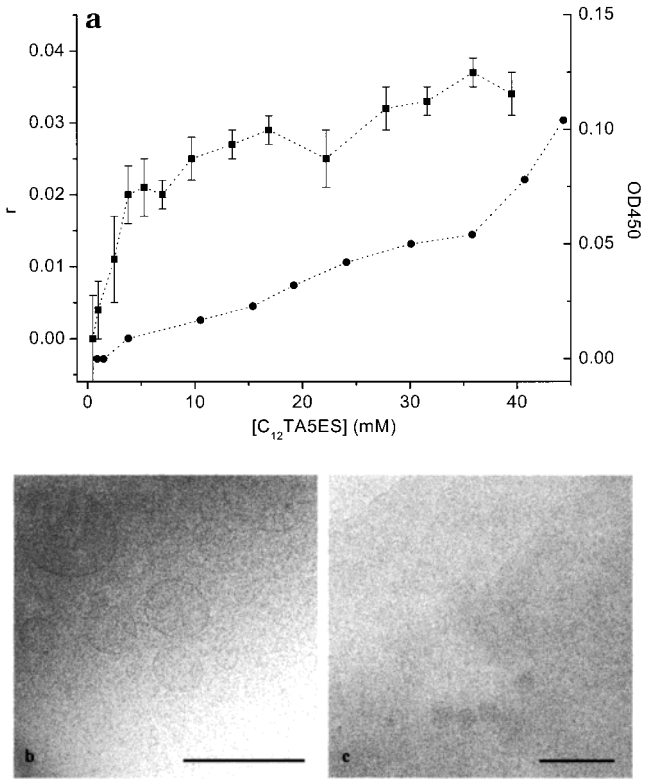

Figure 2. (a) Fluorescence anisotropy of HNC^- (squares, left axis) in aqueous solutions of C_{12}TA5ES and the turbidity of the solutions (circles, right axis). (b) Cryo TEM micrograph of LUVs in a 16 mM C_{12}TA5ES solution. (c) Cryo TEM micrograph of surfactant layers and LUVs as observed in a 54 mM C_{12}TA5ES solution. The bar represents 500 nm.

the fluorescence anisotropy of Sal^- (and thus of 5ES), but the magnitude of the *r* values is smaller than in the case of HNC^-.[33] Therefore it was decided to monitor the fluorescence anisotropy of HNC^- despite the slight influence it might have on the aggregation behavior of C_nTA5ES. The fluorescence anisotropy of HNC^- in viscoelastic solutions of C_{16}TAB and NaSal is about 0.03; without C_{16}TAB it is close to 0.001, indicating that the rotational motion of HNC^- is restricted when bound to (entangled) threadlike micelles.[32] Shikata et al.[32] calculated a rotational relaxation time for the HNC^- anion when it is incorporated in threadlike micelles of 1.5 ns, much longer than that in aqueous solution (0.01 ns).

C_{12}TA5ES. Figure 2a shows both the fluorescence anisotropy of HNC^- in aqueous solutions of C_{12}TA5ES and the turbidity of the solutions. Aqueous solutions of C_{12}TA5ES become slightly turbid beyond the cac. Although the turbidity seems to be small (only 0.01 for 4 mM of C_{12}TA5ES), the solutions are clearly turbid when inspected visually. Upon increase of the C_{12}TA5ES concentration, the solutions show a slight increase in turbidity which becomes more pronounced around 35 mM of C_{12}TA5ES. In addition, the solutions at higher concentrations show an increased viscosity with respect to the lower concentrations. The picture obtained from turbidity experiments is supported by the change of the HNC^- fluorescence anisotropy value *r* in aqueous solutions of C_{12}TA5ES. Below the cac of C_{12}TA5ES the fluorescence anisotropy is close to zero indicating free rotational motion for HNC^-. Around 2 mM of C_{12}TA5ES, the HNC^- fluorescence anisotropy increases and stays at an about constant value around 0.025.

The aggregates formed in aqueous solutions of C_{12}TA5ES have been characterized by cryo TEM. Figure 2b shows large unilamellar vesicles (LUVs) ranging in diameter from 30 to 500 nm in a 16 mM aqueous solution. Cryo TEM was also performed on an aqueous solution of 54 mM of C_{12}TA5ES which is above the transition in the turbidity plot at 35 mM. This technique revealed LUVs ranging in diameter from 40 to 400 nm although the number density of LUVs had decreased with respect to the 16 mM sample. In addition, surfactant layers having a length of more than 3 μm which are arranged like roof tiles are observed (Figure 2c). Those surfactant layers may explain both the increase in turbidity as well as the increase in viscosity of the solutions above 35 mM. The *r* value is not affected by the formation of surfactant layers since the microsurroundings of the probe do not change upon going from vesicles to surfactant layers. In both cases the probe sits in a bilayer environment. The plateau fluorescence anisotropy value of HNC^- in the presence of C_{12}TA5ES bilayers is ca. 0.035 and corresponds well to that of HNC^- in the presence of didodecyldimethylammonium bromide vesicles (DDAB, $r = 0.038$). Aqueous solutions of C_{12}TA5ES do not show viscoelastic behavior analogous to C_{12}TASal although solutions of both surfactants become viscous upon increasing the surfactant concentration. Since the formation of vesicles has not been observed in aqueous solutions of C_{12}TASal, it is concluded that the additional ethyl substituent in $5ES^-$ is responsible for the formation of vesicles in the case of C_{12}TA5ES.

Although vesicles in mixtures of cationic and anionic surfactants with dodecyl chains have been studied frequently,[34] reports on the formation of vesicles in aqueous solutions of single-tailed, unbranched cationic surfactants with a dodecyl chain are quite rare. In a previous study[35] we have demonstrated the formation of vesicles in aqueous solutions of alkyltrimethylammonium−Methyl Orange surfactants where the counterion is also hydrophobic in nature. The formation of vesicles from a single-tailed surfactant with a dodecyl chain has also been reported for the zwitterionic dodecyldimethylamine oxide (C_{12}DAO) amphiphile upon addition of salicylic acid[36] and cinnamic acid.[36,37] This phenomenon was attributed to protonation of C_{12}DAO which than interacts electrostatically with the aromatic counterions, resulting in bilayer instead of micelle formation.

C_{14}TA5ES. Figure 3a shows the fluorescence anisotropy of HNC^- in aqueous solutions of C_{14}TA5ES and the turbidity of the solutions. Aqueous solutions of C_{14}TA5ES become viscoelastic immediately above the cac. The turbidity of the solutions increases around 25 mM, which marks the lower boundary of a two-phase region that extends to about 35 mM. The upper phase is turbid, and the lower one is clear and viscoelastic. Phase separation takes several weeks. Beyond the macroscopic phase-separated region the turbidity increases further whereas the viscoelasticity decreases. When solutions in this concentration range are viewed under a light microscope, the observed vesicles move slowly which is the result of the relatively high viscosity of these solutions. The fluorescence anisotropy value scatters around 0.02 in the

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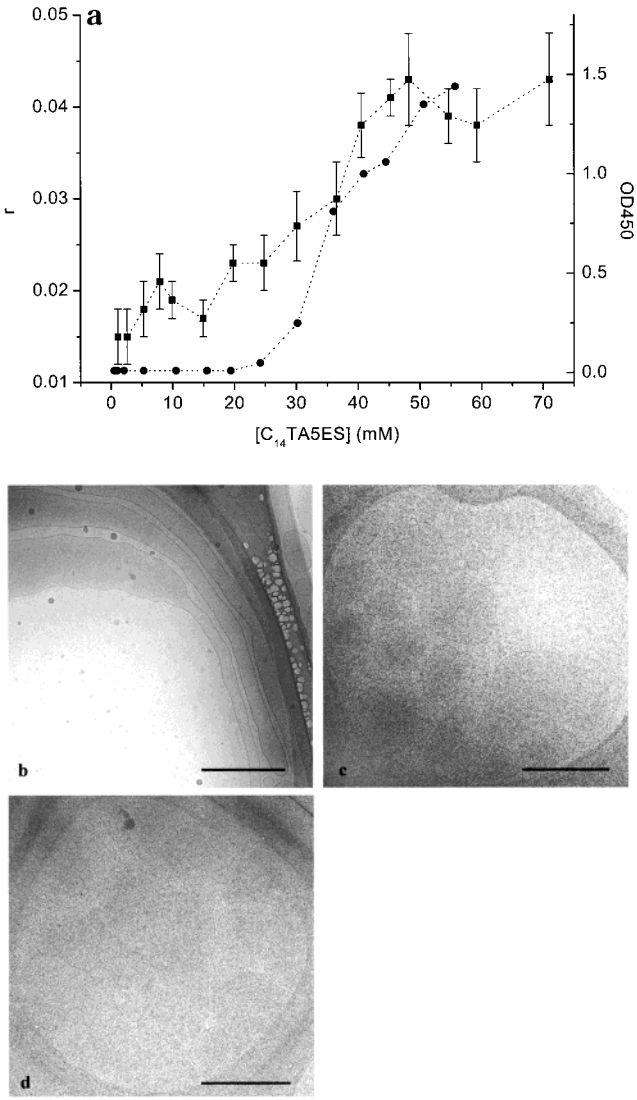

Figure 3. (a) Fluorescence anisotropy of HNC^- (squares, left axis) in aqueous solutions of C_{14}TA5ES and the turbidity of the solutions (circles, right axis). (b) Cryo TEM micrograph of wormlike vesicles in a 12 mM aqueous solution of C_{14}TA5ES. (c) Cryo TEM micrograph of LUVs and LMVs in a 22 mM aqueous solution of C_{14}TA5ES. (d) Cryo TEM micrograph of LUVs, LMVs, and plate structures in a 33 mM aqueous solution of C_{14}TA5ES. The bar represents 500 nm.

concentration region below 35 mM of C_{14}TA5ES and increases to a value around 0.04 at higher surfactant concentrations. Several concentrations of C_{14}TA5ES were studied by cryo TEM which gave the following picture. In the concentration range where the turbidity is small (below 25 mM of C_{14}TA5ES) LUVs and long wormlike vesicles are present in aqueous solution. The about spherical LUVs have a diameter ranging from 150 to 500 nm whereas the wormlike vesicles are longer than 3 μm; their width ranges from 25 to 300 nm. Figure 3b,c shows a representative picture of aggregates formed from C_{14}TA5ES in aqueous solution at concentrations smaller than 25 mM. Aqueous solutions of C_{14}TA5ES in the concentration region above 25 mM contain LUVs ranging in diameter from 150 to 500 nm and large multilamellar vesicles (LMVs) ranging in diameter from 250 to 500 nm. Elongated vesicles are observed as well, although their length has decreased considerably to 600 nm or less. In those samples plate structures are also present which are approximately similar to those observed at high C_{12}TA5ES concentrations. Figure 3d shows structures of C_{14}TA5ES as observed at concentrations above 25 mM. On the basis of cryo TEM experiments, it can be concluded that the increase in turbidity around 25 mM of C_{14}TA5ES is due to a transition from LUVs to LMVs (compare Figure 3c,d). Previously, changes in turbidity have also been attributed to unilamellar-to-multilamellar phase transitions.[38]

Similar to C_{12}TA5ES, no wormlike micelles are observed in aqueous solutions of C_{14}TA5ES although these solutions are viscoelastic. Therefore the viscoelasticity is attributed to the presence of the wormlike vesicles. Usually, viscoelasticity is attributed to entangled wormlike micelles which is indeed the case for C_{14}TASal.[28]

The changes in HNC^- fluorescence anisotropy with increasing concentrations of C_{14}TA5ES are not easy to explain. Below 40 mM of C_{14}TA5ES the *r* value gradually increases from 0.015 to 0.030 whereas it scatters around 0.040 in the concentration region above 40 mM of C_{14}TA5ES. As bilayer structures are present in all solutions investigated, the *r* value would have been expected to reach a plateau value not far beyond the cac (analoguous to C_{12}TA5ES). Since HNC^- is not a commonly used probe for measuring molecular motions in surfactant aggregates, we have measured HNC^- *r* values in various surfactant systems for comparison. Viscoelastic solutions containing C_{14}TAB and sodium salicylate (NaSal) show a rather scattered *r* value between 0.030 $\pm$ 0.014 and 0.047 $\pm$ 0.011, whereas the *r* value in a 20 mM solution of C_{14}TAB was 0.047 $\pm$ 0.016. In a vesicular solution of C_{12}TAB and sodium dodecyl sulfate (SDS) an HNC^- *r* value of 0.123 $\pm$ 0.017 was measured whereas it was 0.038 $\pm$ 0.005 in a DDAB and 0.075 $\pm$ 0.005 in an DODAB (dioctadecyldimethylammonium bromide) environment. In micellar systems the error is larger than in vesicular systems. The *r* value in a DTAB/SDS solution is remarkably large and cannot be attributed to decreased rotational motion of the probe with respect to DDAB or DODAB. Therefore other factors must play a role in catanionic systems.

Morphologies of surfactant aggregates as observed in this study have been found before in e.g. a study of the aggregation behavior of sodium 4-(8-hexadecyl)benzenesulfonate (SHBS).[39] Cryo TEM performed on a 1.7 wt % solution revealed structures such as spherical vesicles but also coiled wormlike vesicles and long tubes (>2 μm). Unfortunately, it was not reported whether those structures have an effect on the viscosity of the solution.

C_{16}TA5ES. Figure 4 shows the fluorescence anisotropy of HNC^- in aqueous solutions of C_{16}TA5ES combined with the turbidity of the solutions. Analogous to C_{14}TA5ES, aqueous solutions of C_{16}TA5ES become viscoelastic immediately above the cac. The turbidity of the solutions is small (ca. 0.05), but it increases around 3 mM. A 4 mM aqueous solution was viewed under an optical microscope which revealed the formation of vesicles ranging in diameter from 5 to 15 μm. Therefore the increase in *r* value is attributed to the fact that HNC^- binds to vesicles which leads to a decrease in its rotational freedom. The viscosity of the solutions decreases significantly upon increasing the surfactant concentration, and above 20 mM the solutions show no viscoelasticy any more. Phase separation in a surfactant-lean lower phase and a surfactant-rich upper phase occurs between 3 and 20 mM. Cryo TEM was performed on an aqueous solution of 15 mM of C_{16}TA5ES and revealed the formation of LUVs

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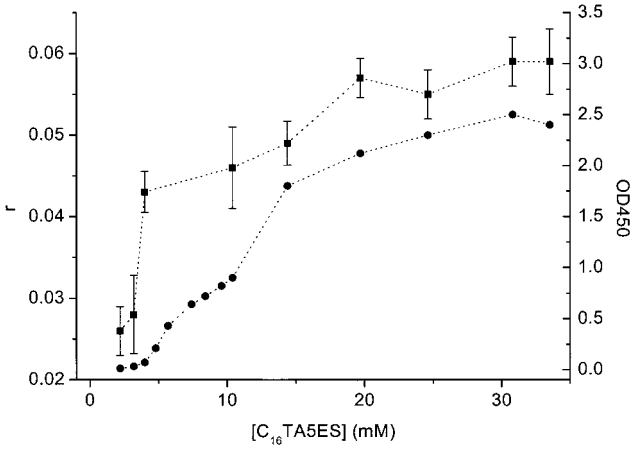

Figure 4. Fluorescence anisotropy of HNC^- (squares, left axis) in aqueous solutions of C_{16}TA5ES and the turbidity of the solutions (circles, right axis).

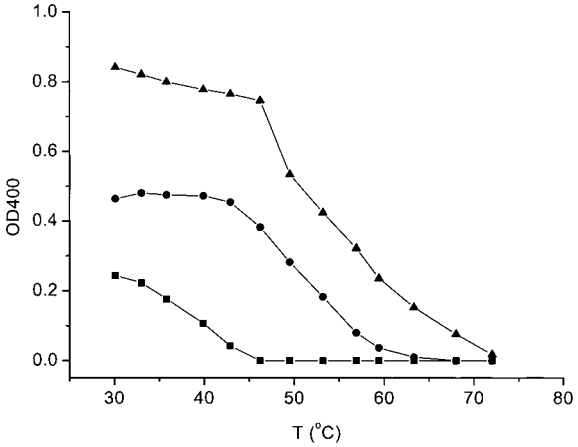

Figure 5. Turbidity of 3.1 mM (squares), 4.2 mM (circles), and 5.2 mM (traingles) aqueous solutions of C_{16}TA5ES as a function of temperature.

and LMVs ranging in diameter from 30 to 200 nm. In addition, elongated and long wormlike vesicles ranging in size from 100 to 400 nm and more than 3 μm, respectively, were observed. These deformed or highly flexible banana-shaped vesicular aggregates have been observed previously in aqueous mixtures of sodium octyl sulfate (SOS) and C_{16}TAB.[5a] The formation of these types of aggregates was explained by a low bending rigidity of mixed membranes and, second, by shear effects during sample preparation.

Similar to C_{14}TA5ES, the viscoelasticity in aqueous solutions of C_{16}TA5ES is attributed to the presence of long wormlike vesicles. Although samples of low C_{16}TA5ES concentration were not studied by cryo TEM, it is assumed that the increase in turbidity around 3 mM is due to the formation of LMVs, analoguous to C_{14}TA5ES.

C_{16}TASal is a well-known wormlike micelle-forming surfactant.[28] Upon increase of the hydrophobic moiety of the counterion from salicylate to 5-methylsalicylate, it was observed that, in combination with C_{16}TAB, vesicles were formed in aqueous solution.[16] This occurred when the mixing ratio of 5-methylsalicylic acid to surfactant was 1.1. In solutions with a smaller mixing ratio spherical and wormlike micelles were formed. Therefore it was not surprising that vesicles are formed in aqueous solutions of C_{16}TA5ES, but the absence of micelles is remarkable. Also C_{16}TAHNC which is a surfactant system similar to C_{16}TA5ES is a vesicle-forming surfactant. HNC^- is an even larger counterion than $5ES^-$.

Note that the HNC^- fluorescence anisotropy plateau value increases from C_{12}TA5ES to C_{14}TA5ES to C_{16}TA5ES reflecting the increase in packing efficiency of the surfactant molecules in the membrane upon increasing alkyl chain length. This is confirmed by the fact that the fluorescence anisotropy value of HNC^- is lower when the probe is bound to vesicles formed from DDAB (0.038) than that of HNC^- bound to DODAB vesicles (0.075).

Temperature-Dependent Aggregation Behavior of C_{16}TA5ES. Figure 5 shows the turbidity of aqueous solutions C_{16}TA5ES at different concentrations as a function of temperature. The solutions undergo a transition from a turbid phase at 30 °C to a clear viscoelastic phase at higher temperatures. The transition temperature increases upon increasing concentration of C_{16}TA5ES. Analogous to C_{16}TAHNC,[20] the turbidity changes are attributed to a vesicle-to-micelle transition. In the case of C_{16}TAHNC the transition was explained by increasing solubility of the HNC^- counterion upon increasing temperature; i.e., the counterion binding decreases upon increasing temperature.[22] This leads to increased headgroup repulsions and an increase in aggregate curvature, and therefore, vesicles are transformed into the next homologue in the aggregate curvature series which are wormlike micelles. Horbascheck et al.[21] studied aqueous solutions of C_{16}TAHNC by DSC. They found a transition at 46 °C ($\Delta H° = 0.5$ kJ mol^{-1}) independent of the surfactant concentration and attributed it to a transition within the vesicular phase. In addition, they observed an increase in conductivity of C_{16}TAHNC as well as of KCl entrapped in C_{16}TAHNC at the transition temperature revealed by DSC. Temperature-induced micelle-to-vesicle transitions are well-known for nonionic surfactants. In these cases the change in aggregate shape is attributed to a decrease in headgroup hydration upon increasing temperature leading to a decrease in effective headgroup area. Moreover, the hydrocarbon chains become less ordered upon increasing temperature (compare the phase transition temperature below which the alkyl chains are in a more ordered state). Consequently, an increase in temperature leads to an increase in the packing parameter value which favors bilayer formation.[40] On the other hand, headgroup areas of ionic surfactants are only slightly affected by a change in temperature.

Conclusions

We have studied the phase behavior of a series of C_nTA5ES (n = 12, 14, 16) surfactants. Unlike their salicylate counterparts they do not form wormlike micelles, rather the formation of vesicular phases is observed. Aqueous solutions of C_{12}TA5ES contain LUVs which transform into surfactant layers upon increasing the surfactant concentration. Those solutions are viscous. C_{14}TA5ES and C_{16}TA5ES form LUVs at low surfactant concentrations, and both show a transition to LMVs upon increasing surfactant concentration. Viscoelasticity in the solutions is attributed to the prescence of long (>3 μm) wormlike vesicles.

Cacs of the novel surfactants are smaller than those of their salicylate analogues.

Upon the heating of aqueous solutions of C_{16}TA5ES, a transition from a turbid phase to a clear viscoelastic phase is observed. This phenomenon is attributed to a vesicle-

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to-micelle transition which results from decreased counterion binding upon increasing the temperature.

It is remarkable how sensitive the morphological preferences of the aggregates are to small structural changes in the aromatic counterion.

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